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**GRAFTING OF 2(2-HYDROXY-5-VINYLPHENYL)2H-
BENZOTRIAZOLE ONTO POLYMERS WITH ALIPHATIC GROUPS**

**SYNTHESIS AND POLYMERIZATION OF
2(2-HYDROXY-5-ISOPROPENYLPHENYL)2H-BENZOTRIAZOLE**

AND

A NEW SYNTHESIS OF 2(2-HYDROXY-5-VINYLPHENYL)2H-BENZOTRIAZOLE



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**(NASA-CR-165016) GRAFTING OF 2
(2-HYDROXY-5-VINYLPHENYL) 2H-BENZOTRIAZOLE
ONTO POLYMERS WITH ALIPHATIC GROUPS.
SYNTHESIS AND POLYMERIZATION OF 2
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ABSTRACT

Successful grafting of 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole onto saturated aliphatic C-H groups of polymers has been accomplished. When the grafting reaction was carried out in chlorobenzene at 150-160°C with di-tertiary-butylperoxide as the grafting initiator, grafts as high as 20-30% at a grafting efficiency of 50 and 80% have readily been obtained. It was very important to carry out the grafting reaction in tubes sealed under high vacuum since trace amounts of oxygen cause complete inhibition of the grafting reaction by the phenolic monomer. Grafting reactions were carried out on a variety of different polymers including atactic polypropylene, ethylene/vinyl acetate copolymer, poly(methyl methacrylate), poly(butyl acrylate), and polycarbonate.

2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole was synthesized in nearly 40% yield starting from o-nitroaniline. Diazotization in aqueous HCl gave the diazonium salt which was condensed with p-hydroxyacetophenone to form the azo compound which was reduced to 2(2-hydroxy-5-acetylphenyl)2H-benzotriazole with zinc powder in sodium hydroxide solution. This compound was acetylated and reacted with methyl Grignard reagent to form 2[2-acetoxy-5(2-hydroxy-2-propyl)phenyl]2H-benzotriazole which was then dehydrated with KHSO₄ to the desired 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole. This monomer did not homopolymerize, but was readily copolymerized with styrene, methyl methacrylate and n-butyl acrylate using azobisisobutyronitrile as the initiator. 2(2-Acetoxy-5-acetylphenyl)2H-benzotriazole was also reduced with sodium borohydride to form 2[2-acetoxy-5-(1-hydroxyethyl)phenyl]2H-benzotriazole which was then dehydrated and hydrolyzed to the well known 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole. This latter synthesis provides a novel and probably simpler synthesis of this monomer.

RESULTS AND DISCUSSION

It was demonstrated that 2H5V could be grafted onto aliphatic portions of saturated polymers such as PP, PE-co-VA, PMMA, PBA, and PC. Grafting attempts onto PA-6 were unsuccessful in these preliminary experiments. (Equation 1).

In preliminary experiments it had been established that 2H5V has reactivity in radical polymerization comparable to styrene which was determined in copolymerization experiments of 2H5V with styrene and methyl methacrylate. Initial grafting experiments were therefore carried out with styrene as the grafting monomer in order to establish the appropriate reaction conditions for grafting of 2H5V. It was found that styrene could be grafted effectively to atactic PP if high temperatures and short reaction times were used, so DTBP was used in the temperature range of 150-170°C. These reactive conditions effectively abstract the hydrogen from the aliphatic C-H group. The two aromatic solvents, chlorobenzene and dichlorobenzene, were used since their boiling points lie within the temperature range in question.

Grafting of styrene onto atactic PP with a molar ratio of styrene to PP of 4:1 was initially carried out at polymer concentrations of 10% in dichlorobenzene with DTBP as the initiator from 150 to 160°C. with a reaction time of 24 hrs. This grafting reaction was easily accomplished in an open reaction vessel with nitrogen purge. Under these reaction conditions 5-10% of styrene was grafted at a grafting efficiency of 25-50% without apparent molecular weight degradation or crosslinking. PP-g-S was easily isolated by precipitation from chlorobenzene into acetone. Some homopolymer of styrene was also formed during this reaction but could easily be separated by precipitation of the mother liquors into methanol.

Attempts to obtain PP-g-2H5V under these reaction conditions, namely in an open reaction vessel but under nitrogen atmosphere were unsuccessful with no PP-g-2H5V or poly-2H5V formed.

It became apparent that the difference in the reactivity of styrene and 2H5V could be attributed to the small amounts of oxygen which could not be avoided in an open vessel. Sensitivity of radical vinyl polymerizations to free phenol groups in the monomer has been observed in the past and phenolic OH groups were held responsible. We have, however, shown that oxygen radicals in polymerizations but not for carbon radicals, particularly not for resonance stabilized carbon radicals are susceptible for termination of phenolic-OH groups.

It was therefore decided to carry out the grafting reactions by exclusion of oxygen, e.g., in sealed polymerization tubes where the contents of the tubes were carefully degassed prior to sealing. The workup of the reaction mixture was very simple as the polymer fractions with different degrees of grafting also have different solubility. The effectiveness of the grafting reaction depends also on the solvent selection.

When the reactions were carried out under carefully prepared conditions where the polymerization tube contents were degassed by the freeze-thaw technique and the reaction vessel sealed at less than 0.1 mm, the grafting reaction proceeded smoothly. As shown in Table 1, it was possible to isolate the grafted polymer by precipitation in either acetone or methanol. Polymers with lower amounts of grafting were isolated by precipitation into acetone, while polymers with higher grafting were precipitated by pouring the mother liquors into methanol. As increasing

amounts of 2H5V are grafted onto the polymers, the solubility of the graft copolymers increases in polar solvents like acetone and methanol. It should be recalled that poly-2H5V is soluble in acetone. By elemental analysis, particularly nitrogen analysis, the efficiency of grafting was determined. The grafting efficiency was 75% for PP and as low as 36% for PC. In most cases of PP-g-2H5V and PE-co-VA-g-2H5V, it was possible to obtain polymers which had various amounts of 2H5V grafted onto the polymer.

Preliminary characterization by DSC indicated that the grafted polymer of PP-g-2H5V is quite homogeneous and only one T_g was observed at -13 to -14°C . This is a few degrees higher than the T_g observed for the same batch of atactic polypropylene (-20°C .). No T_g was observed in the region of 100 – 200°C . where the T_g of poly-2H5V was expected which suggested that many small grafts or even single individual attachments of 2H5V may have been formed, rather than long chains of poly-2H5V attached onto a few places of the backbone chain. Preliminary GPC analysis also indicated that PP-g-2H5V is homogeneous and does not seem to contain homopolymer of 2H5V (Figure 1); the M_w is 15,580 and M_n is 7090 with a M_w/M_n of 2.20.

It is concluded that grafting of 2H5V onto a number of polymers has been accomplished. Further characterization of the materials particularly their behavior under ultraviolet aging conditions, and the characterization of their UV spectra is now underway and will be reported in a later paper.

EQUATION 1

Grafting of 2(2-Hydroxy-5-Vinylphenyl)2H-Benzotriazole
onto Saturated Polymers Exemplified by a $-\text{CH}_3$ Group

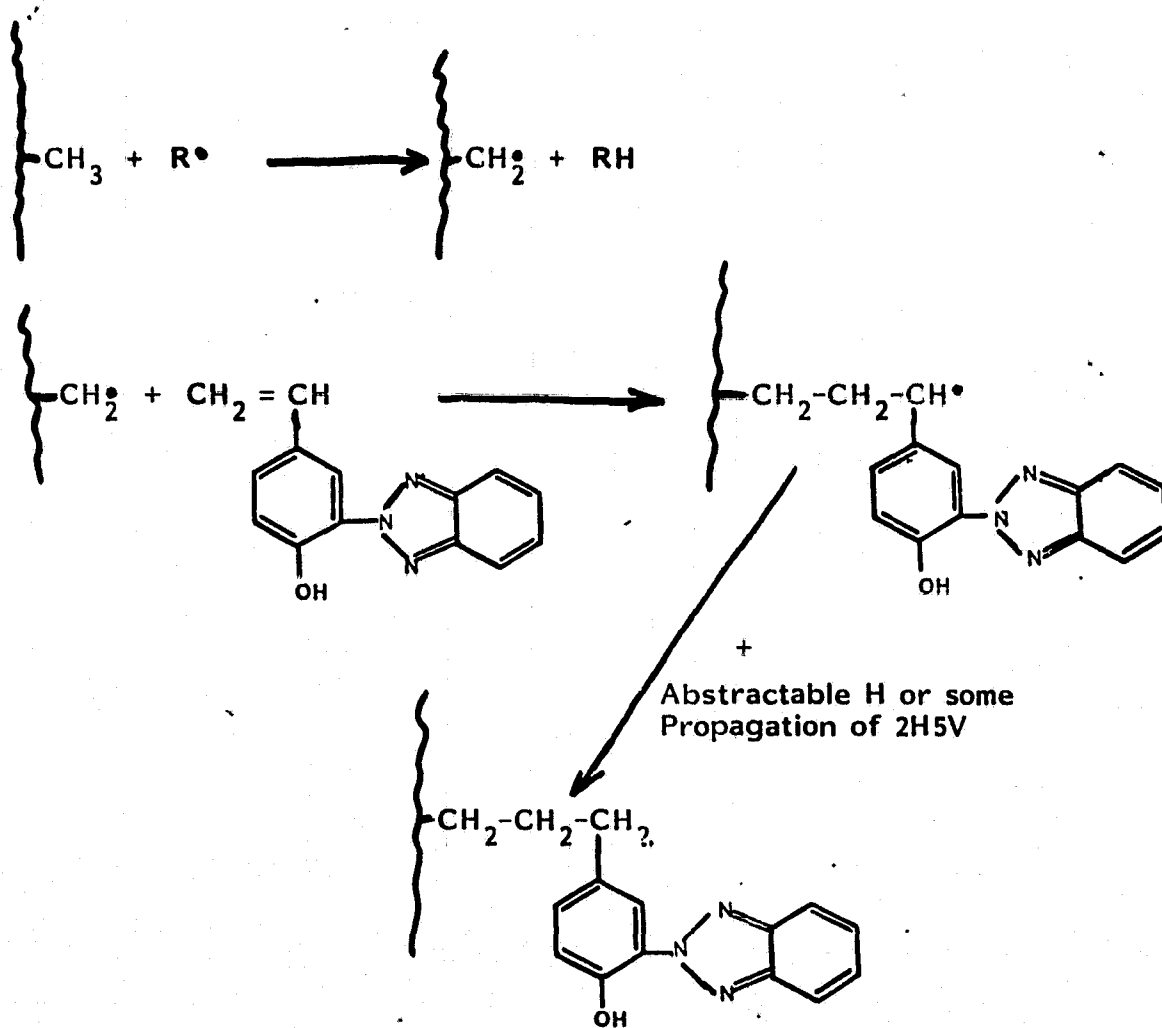


TABLE 1

Results of Grafting of 2-(2-Hydroxy-5-Vinylphenyl)2H-Benzotriazole onto

PP, PE-co-VA, PMMA, PC, PBA, PA-6

Solvent: Chlorobenzene; Amount of Di-tert.-Butyl Peroxide: 2 wt %;
Temperature: 150°C.; Time: 24 hrs.

Polymer Concentration (%)	PP (atactic)	PE-co-VA (Elvax 150)	PMMA (MW=12000)	PC(a)	PBA	PA-6(b)
Molar Ratio, Polymer/2H5V	13.5 4/1	10 4/1	15 4/1	10 5/1	10 4/1	10 4/1
Precipitated in Acetone						
Yield (%)	48(c)	65	—	—	—	73
Contents of 2H5V (mole %)	19	12	—	—	—	0
Precipitated in Methanol						
Yield (%)	16	15	85	80	54	0
Contents of 2H5V (mole %)	37	39	17	7.5	17	0
Grafting Efficiency (%)	75	68	72	36	46	0

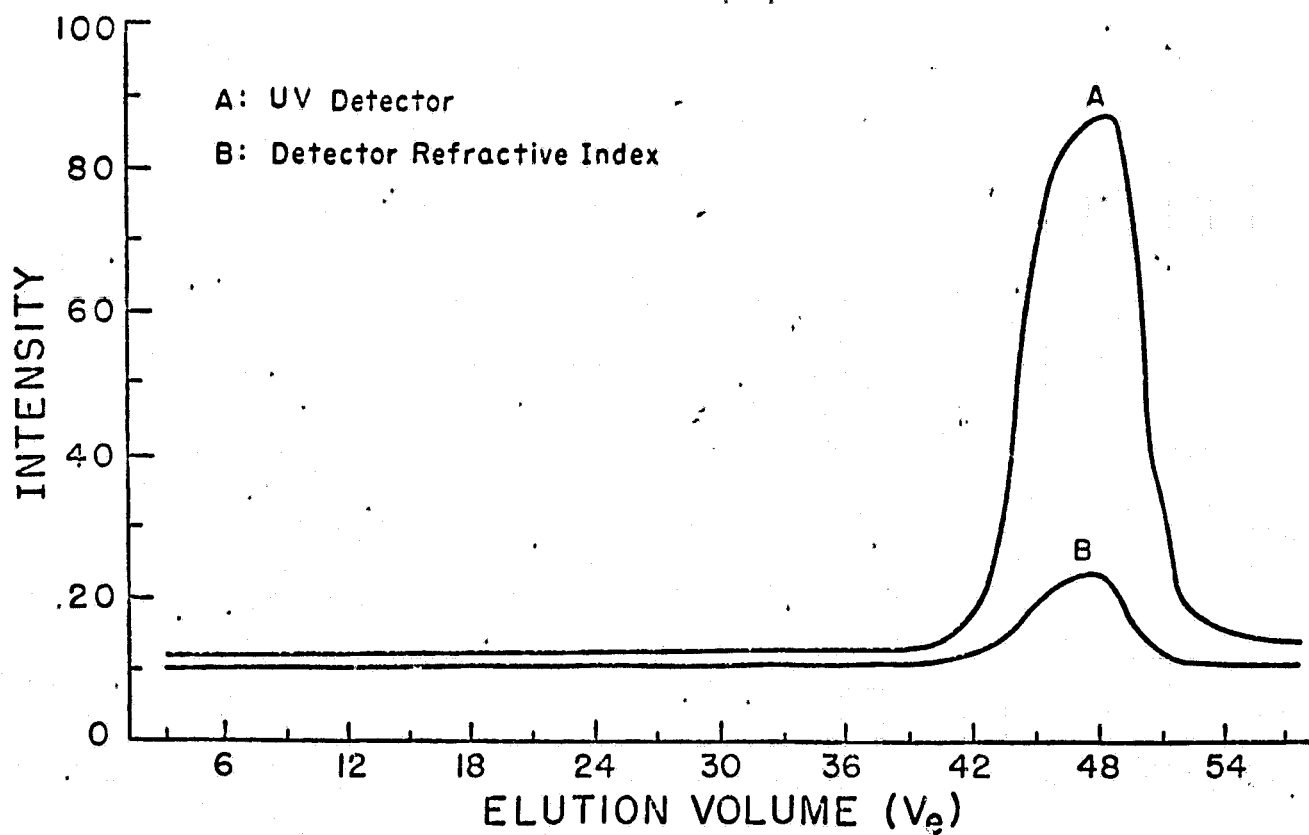
(a) Time: 36 hrs.

(b) Solvent m-chlorophenol

(c) 16% of the starting material was insoluble in the reaction mixture

FIGURE 1

GPC Traces of Poly[(atactic)-propylene-g-2(2-Hydroxy-5-Vinylphenyl)2H-Benzotriazole]



2H5P was synthesized in a sequence of 5 steps in 40% yield. The homopolymerization of 2H5P was attempted, but only its copolymerization was successful. The synthesis strategy provided a key intermediate, 2A5A, which was used for a new and improved method of synthesis 2H5V.

The synthesis of our first intermediate, 2H5A, in the synthesis of 2H5P, required the condensation of diazotized o-nitroaniline in concentrated HCl solution at 0°C. The azo coupling of the diazonium salt with p-hydroxyacetophenone was carried out by dissolving p-hydroxyacetophenone in sodium hydroxide solution to which an excess of sodium carbonate was added. Upon the slow addition of the cold diazonium salt solution to the basic p-hydroxyacetophenone solution, a deep red color was formed which was followed by precipitation of a crystalline material. The temperature was kept below 20°C along with mechanical mixing. After 2 hours, the azo compound was isolated in a yield of 92-95%. The reaction sequence was continued by adding additional sodium hydroxide to dissolve the azo compound. The reductive cyclization of the azo compound with zinc powder to 2H5A proceeded as described for the reduction of the azo compound to 2H5E. (The acetyl carbonyl group was not reduced under these conditions). It was necessary that the reaction temperature for cyclization be kept between 50 and 70°C for at least 4 hours (Equation 1). It was observed that it made little difference whether the sodium hydroxide and the zinc powder were added in one or several portions. The product 2H5A was obtained by

acidification of the phenolate solution with the 2H5A precipitating immediately. The cyclization of the azo compound to form the triazole ring was also carried out with sodium dithionite, but this reaction did not show an improvement in yields nor was it simpler than the zinc/sodium hydroxide reduction. The crude reaction product of 2H5A could be acetylated without further purification.

The acetylation of 2H5A was carried out with an acetic anhydride/pyridine mixture (88:12). After 4 hours of holding the reaction mixture at reflux, 2A5A was obtained in 90-95% yield. Crude 2A5A product precipitated from ice water and was recrystallized from methanol with a melting point of 146-147°C. Attempts to acetylate with acetic anhydride/sulfuric acid always required purification of crude 2A5A by distillation with the product consisting primarily of 2H5A even though care was taken that the sulfuric acid residue was neutralized with sodium acetate before workup. The overall yield from o-nitroaniline to 2A5A was 45-50%. 2A5A is the key intermediate for the synthesis of both of the desired monomers: 2H5P and 2H5V (Equation 2).

Synthesis of 2(2-Hydroxy-5-Isopropenylphenyl)2H-Benzotriazole (2H5P) and
2(2-Hydroxy-5-Vinylphenyl)2H-Benzotriazole (2H5V)

Purified 2A5A served as the starting material for the two carbinols (Equation 2). 2[2-Hydroxy-5-(2-hydroxy-2-propyl)phenyl] 2H-benzotriazole (2H5PR) was obtained in 87-90% yield by Grignard methylation with methyl magnesium iodide. 2A5A is not very soluble in diethyl ether, therefore, THF was used as the solvent for 2A5A while diethyl ether was used as the solvent for the Grignard reagent. The product (2H5PR) was a pale, yellow solid, m.p. 128-129°C. Recrystallization of this carbinol is somewhat difficult, but could be accomplished from either cold ether or cold n-hexane. The purification is not crucial at this point as crude 2H5PR can be directly dehydrated. The dehydration reaction in the presence of potassium hydrogen sulfate proceeded smoothly by distillation in a short path distillation apparatus (Kugelrohr). No stabilizer (radical scavenger) is needed for the distillation of 2H5P. For the synthesis of most other UV polymerizable stabilizers, picric acid had to be added in the last reaction step that formed the vinyl compounds to avoid polymerization of the vinyl monomer. It was concluded that 2H5P is a stable monomer which can be distilled and stored with no special precautions. 2H5P could also be recrystallized from n-hexane or methanol or could be sublimed.

The sodium borohydride reduction of 2A5A is a relatively easy reaction, but leads to a mixture of products: 2[2-hydroxy-5-(1-hydroxyethyl)phenyl]2H-benzotriazole and 2[2-acetoxy-5-(1-hydroxyethyl)phenyl]2H-benzotriazole in a ratio of about 4:1 under our conditions. The reduction products were obtained

in high yield. Dehydration of the mixture to 2H5V and 2A5V was carried out with KHSO_4 . Sodium borohydride reduction and dehydration had an overall yield of about 85-90% which gives a total yield of a mixture of 2H5V of about 40% based on o-nitroaniline. In this case, the dehydration had to be carried out in the presence of picric acid to avoid polymerization. To obtain pure 2H5V the mixture had to be hydrolyzed. It does not make any difference if the hydrolysis is done before or after the dehydration step as both methods were tried and worked satisfactorily. 2H5V can be readily crystallized from methanol/water (9:1) or from pure methanol and gives white needles; m.p.: 98-99°C.

All intermediates of the syntheses were characterized by elemental analysis, infrared, ^1H and ^{13}C NMR spectra. Infrared spectra of the key intermediates 2H5A (Figure 1) and 2H5P (Figure 2) are typical for these compounds. ^1H NMR spectra of 2H5A (Figure 3) and 2H5P (Figure 4) showed typical chemical shift values which are consistent with the proposed structure. ^1H chemical shift data of all important compounds synthesized in this work are shown in Table 1. ^{13}C NMR spectra of 2H5A (Figure 5) and 2H5P (Figure 6) show chemical shifts whose numeric numbers are presented in Table 2.

Other Attempts to Synthesize 2(2-Hydroxy-5-Isopropenylphenyl)2H-Benzotriazole

The synthesis of 2H5P via the condensation of the diazonium salt of o-nitroaniline with other appropriately substituted p-phenols has not been successful. One of the attempts to introduce the isopropenyl group in the 5 position (para position to the phenolic OH group) of 2(2-hydroxyphenyl)-

2H-benzotriazole was the use of 2(2-hydroxy-5-isopropylphenyl)2H-benzotriazole as the starting intermediate. The compound was also readily acetylated but it was impossible to brominate this compound in the methine position of the isopropyl group under conditions similar to those successfully used for the bromination of the α -hydrogen in an ethyl group attached to the benzene ring. For NBS brominations, aromatic isopropyl groups have been described as sterically hindered and consequently impossible to brominate. Attempts to brominate the model compound p-isopropylphenyl acetate under normal NBS bromination conditions, were also unsuccessful.

Another attempt at the direct synthesis of 2H5P was again from 2(2-acetoxy-5-isopropylphenyl)2H-benzotriazole. Attempted oxidation with potassium permanganate solution gave in low yield oxidation products which could not be identified by TLC and NMR and did not contain the expected 2(2-hydroxy-5-(2-hydroxy-2-propyl)phenyl)2H-benzotriazole. Synthesis of 2H5P via the oxidation route from 2(2-hydroxy-5-isopropylphenyl)2H-benzotriazole by peroxidation is still a possible route to 2H5P.

The condensation of the diazonium salts of o-nitroaniline with other p-substituted phenols such as 4-(2-hydroxy-2-propyl)phenol or directly with p-isopropenylphenol looked attractive and could give the desired 2H5P directly in one or two steps (Equation 3). Using Bisphenol A as the starting material (which is known to be susceptible to carbon carbon cleavage between the para carbon atom in the aromatic ring and the 2-carbon atom of the propyl group in the presence of alkali) gave p-isopropenylphenol in 85% yield. The coupling

reactions of the diazonium salt of o-nitroaniline with either 4-(2-hydroxy-2-propyl)phenol (which was prepared by Grignard methylation of p-acetoxyacetophenone) or coupling with 4(1-hydroxy-1-ethyl) phenol, (obtained by sodium borohydride reduction from the same starting material), gave azo compounds which upon reductive cyclization, yielded at least two products (as judged by TLC). One of the products was identified and characterized as 2(4-hydroxyphenyl)2H-benzotriazole (4H), m.p. 230°C. Coupling reactions where the diazonium ion attacks the para position to the phenolic OH group with substitution in p- α -alkylcarbinols groups have been described in the literature before.

Attempts were made to couple p-isopropenylphenol with the diazonium salts of o-nitroaniline. Under normal conditions an azo compound was obtained which was reductively cyclized with zinc/sodium hydroxide. After acidification of the phenolate, a 50-60% yield of a mixture of crude products was obtained which could not be identified but was not either of the two expected compounds of 2H5P or 4H.

We have also attempted to carry out a "benzotriazolization" of Bisphenol A with the diazonium salt of o-nitroaniline (Equation 4). In principle, the expected 2H5P could be obtained by pyrolysis of benzotriazolized Bisphenol A. If a bisbenzotriazolization on both benzene rings occurred, on pyrolysis of this compound one would have expected to obtain 2H5P or 4H. 4H is very difficult to prepare directly, as "benzotriazolization" of phenols which are not substituted in the para-position always causes para-condensation

rather than ortho condensation. The benzotriazolization product of Bisphenol A could serve as a conventional low molecular weight UV absorber, as well as an intermediate for the synthesis for benzotriazole type polymerizable UV absorbers. After the proper reductive cyclization of the azo compound, a benzotriazolized product was obtained in about 80-85% yield. When this crude product was pyrolyzed in the presence or absence of sodium hydroxide, a crystalline material, m.p. 228-230°C was obtained which was identified and characterized as 4H. On the basis of these results we assume that 4H was obtained directly, as we had seen in the past, by substitution of the p-isopropylphenol group by the diazonium salt.

These results show that aliphatic substituents in para-position of the phenolic OH group can be readily displaced by diazonium salts, in our case that of o-nitroaniline.

Preparation and Characterization of Polymers of 2(2-Hydroxy-5-Isopropenyl-phenyl)2H-Benzotriazole

With the experience that has been gained in our laboratory on the polymerization of 2H5V and the grafting of 2H5V, the polymerization, copolymerizations and grafting of 2H5P were investigated. Reaction conditions required the complete exclusion of oxygen from the reaction vessel which meant that the reaction had to be carried out in sealed tubes at a reduced pressure of about 0.005 mm (Equation 5). The results of the copolymerizations with MMA, BA and St are summarized in Table 3.

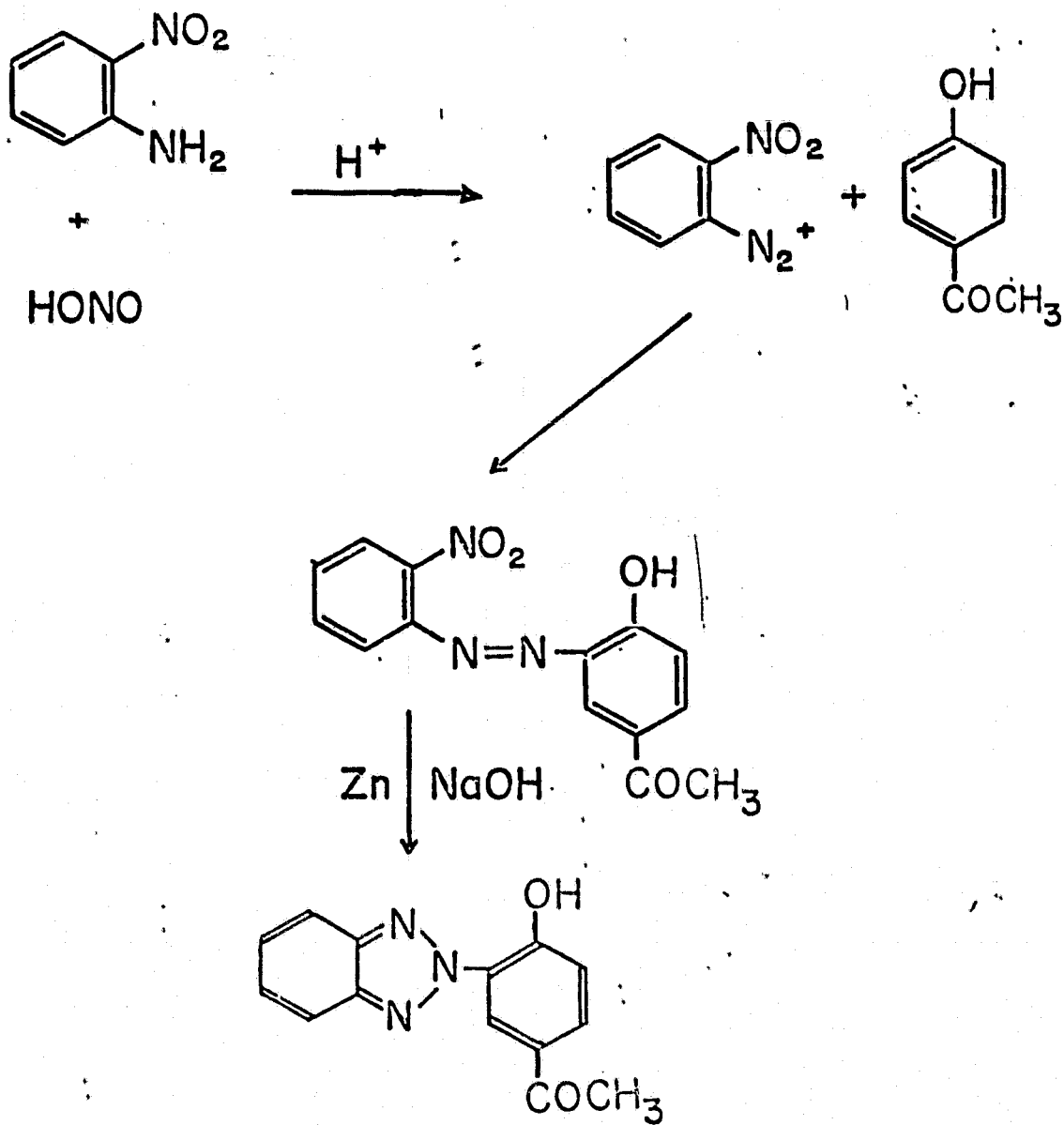
All attempts to homopolymerize 2H5P in concentrated toluene solutions with AIBN as the initiator were unsuccessful. Concentrations of 0.83 moles per liter and 2.5 moles per liter of 2H5P were used at reaction temperatures of 50 and 60°C. In both cases, only the starting product, 2H5P, could be recovered. These results illustrate the most important difference between the two monomers 2H5P and 2H5V - 2H5P has no tendency to homopolymerize, but under similar conditions homopolymerization of 2H5V readily occurs. 2H5P is an α -methylstyrene derivative while 2H5V is a styrene derivative. It is known that the ceiling temperature of α -methylstyrene is 61°C while the ceiling temperature of styrene is in excess of 300°C. As a consequence, it is not surprising that 2H5P does not homopolymerize, at least not at 50 to 60°C in dilute solution. That does not exclude the possibility that the homopolymerization of 2H5P could be achieved at much lower temperatures. It is also worth noting that solvents

used to dissolve 2H5P would further lower the ceiling temperature of polymerization.

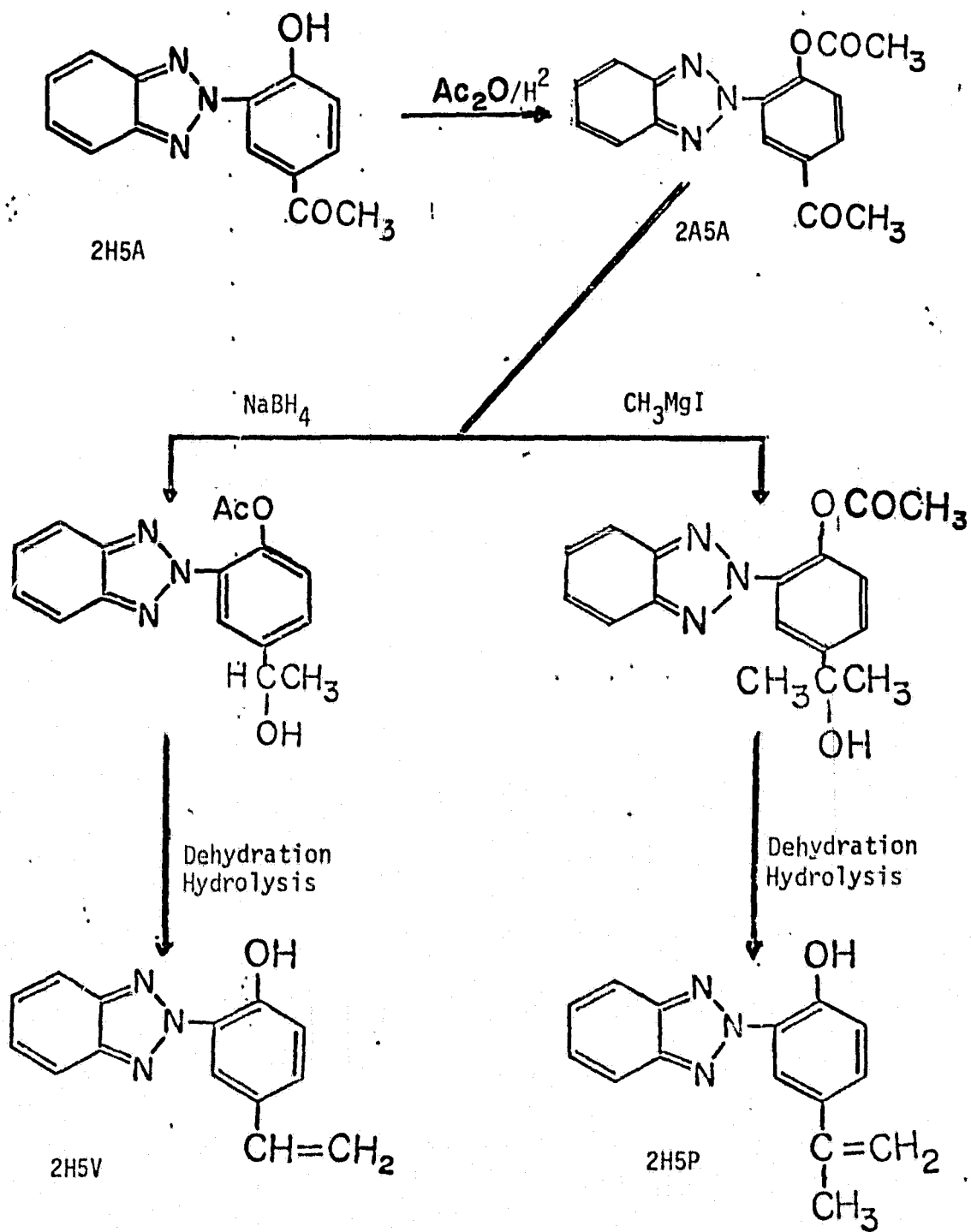
2H5P was successfully copolymerized with MMA and BA to polymer compositions that have a greater amount of 2H5P incorporated into the polymer than 2H5P in the monomer feed ratio. Styrene monomer could be used as its own solvent for copolymerization with 2H5P, and 2H5P is readily incorporated (Table 3) into the copolymer.

In conclusion, 2H5P was synthesized as a new polymerizable UV absorber. This propenyl monomer is less reactive than the vinyl compound toward polymerization. It does not homopolymerize, but readily copolymerizes with conventional resonance stabilized comonomers. This characteristic is substantially different from the characteristics of 2H5V which readily homopolymerizes and has to be stabilized with radical inhibitors to maintain it in the monomeric form. 2H5P in initial experiments has shown no tendency to graft onto normal hydrocarbon polymers such as atactic polypropylene, poly(ethylene-co-vinyl acetate), poly(n-butyl acrylate) and poly(methyl methacrylate), as well as polycarbonate.

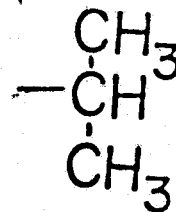
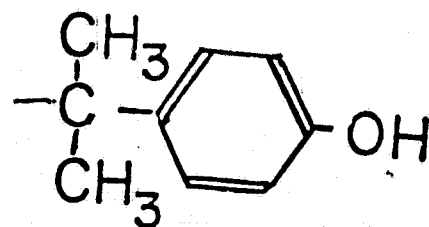
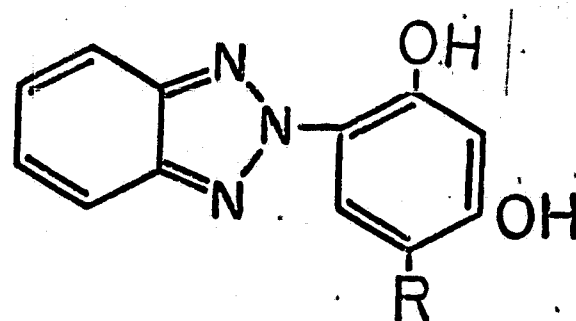
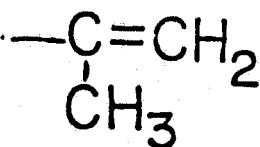
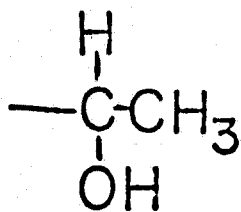
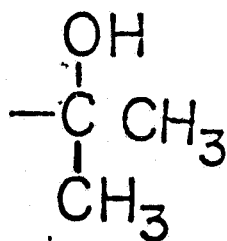
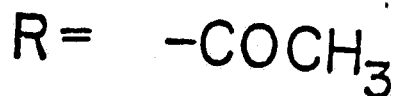
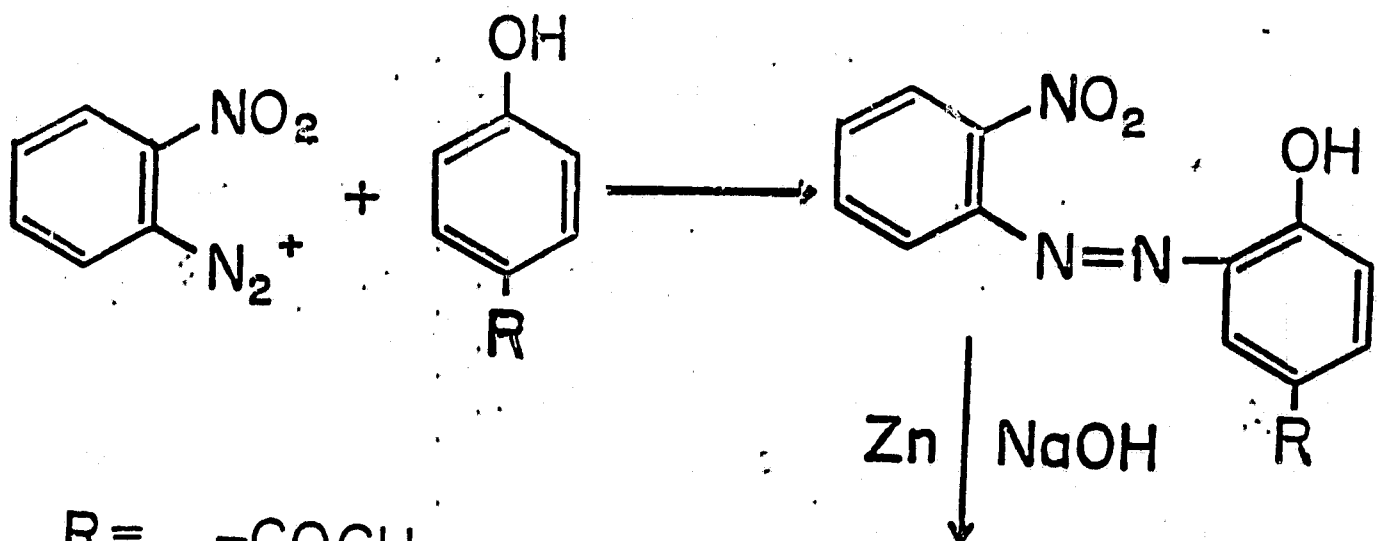
EQUATION 1

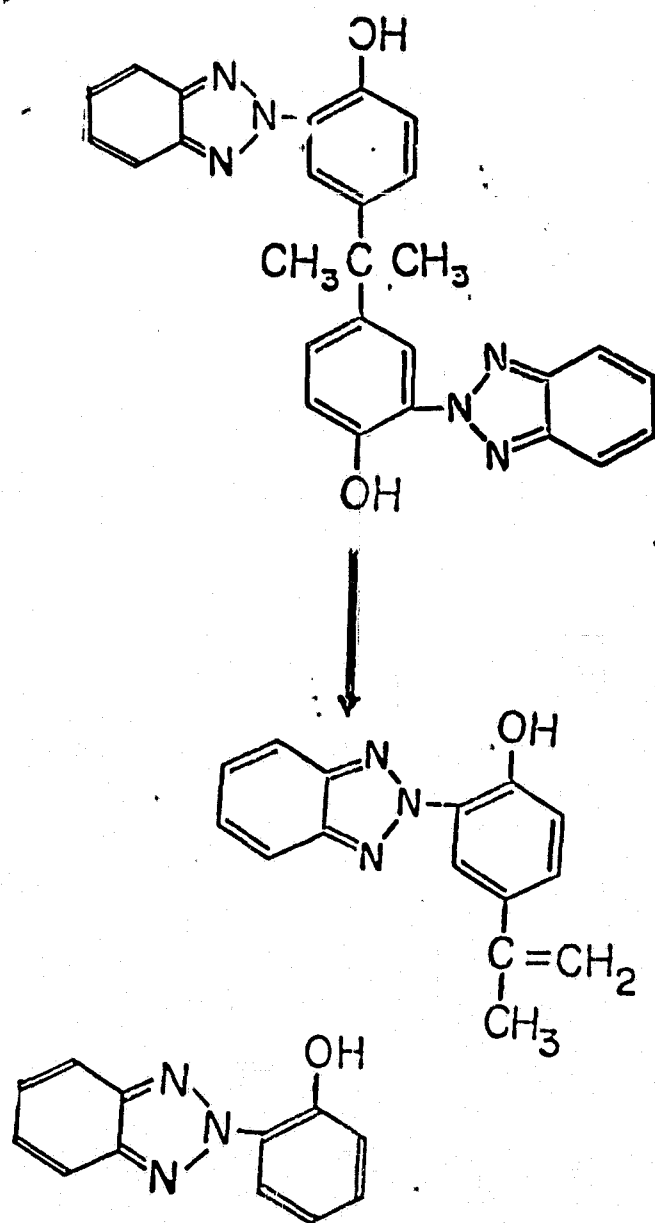
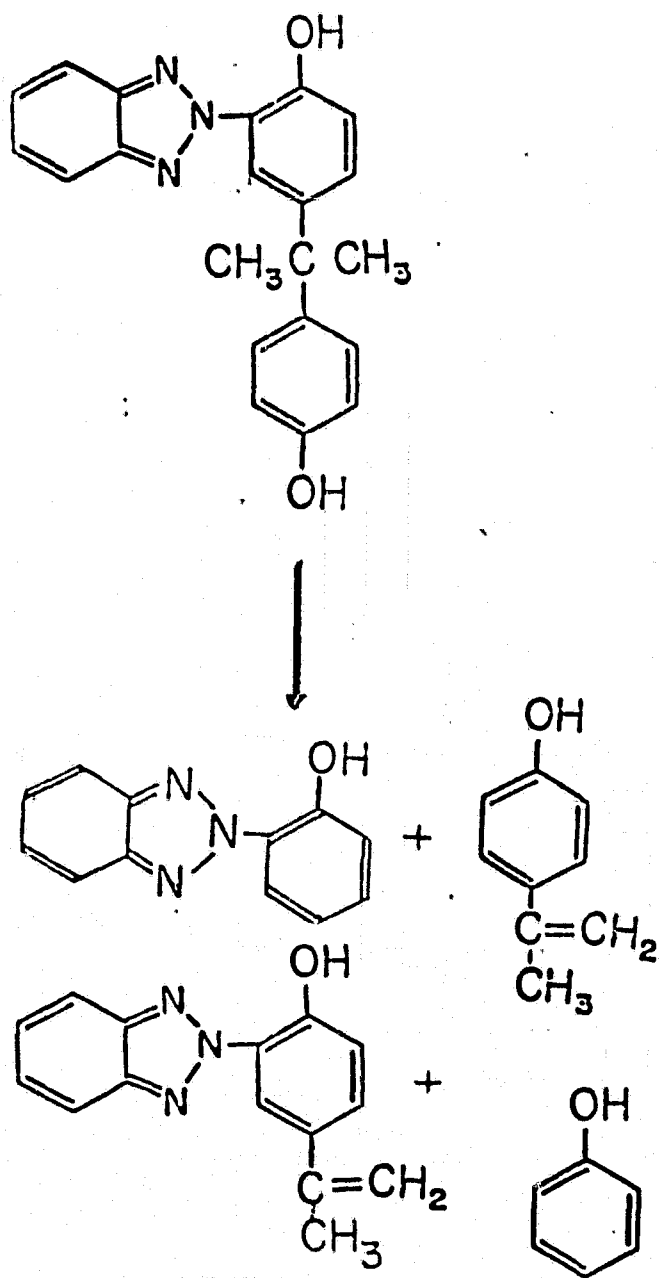
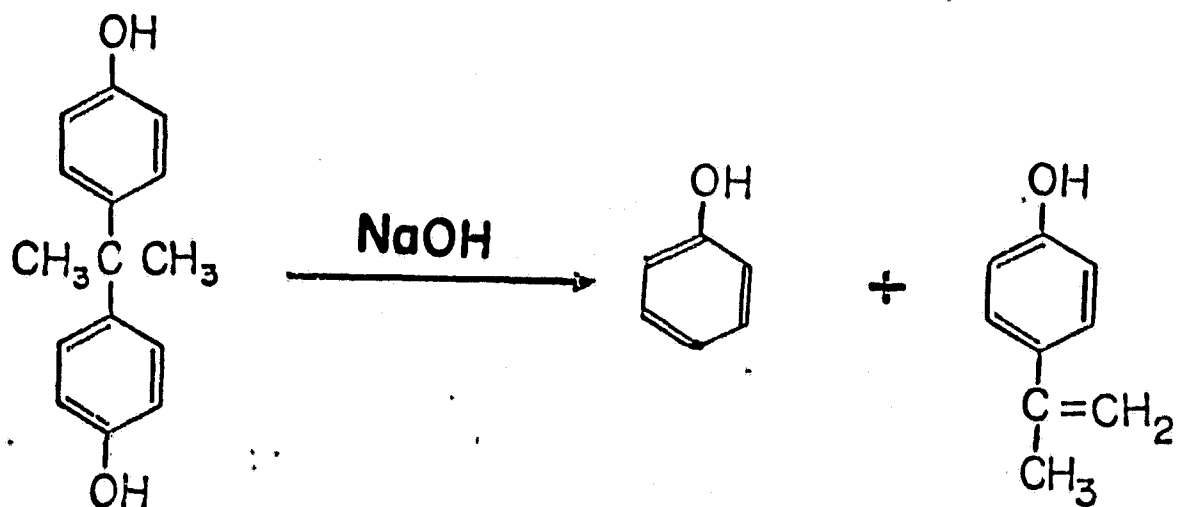


EQUATION 2



EQUATION 3





EQUATION 5

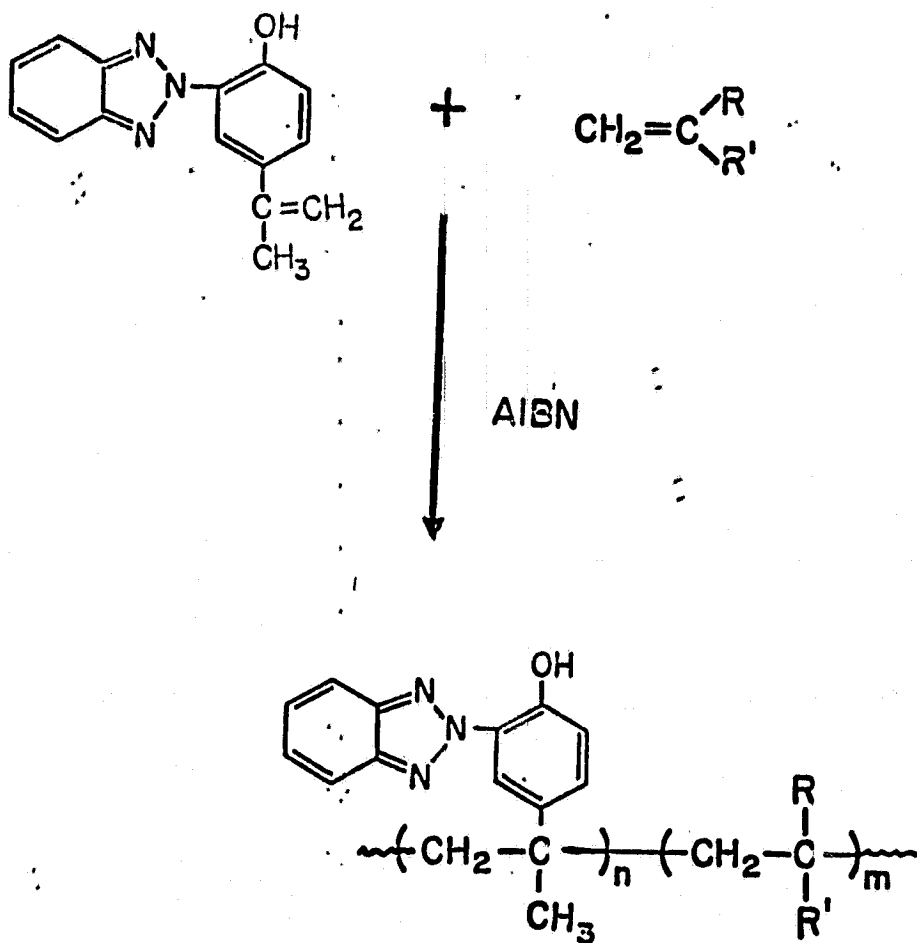


TABLE 3

Polymerization of 2(2-Hydroxy-5-Isopropenylphenyl)2H-Benzotriazole

Polymerization conditions: Initiator: AIBN, 0.2 mole %, Temperature 60°C, Time, 2.5 days, Sealed Tube.

2H5P		Comonomer		Total Amount of Monomers		Solvent		Polymer yield in g	Polymer Comp. 2H5P units	η_{inh} dL/g
in g	in mmole	Type	in g	in mmole	in g	type	Amount in ml			
1.26	5.0	—	—	—	1.26	5.0	toluene	2	(a)	—
2.82	11.2	MMA	6.42	64.1	9.24	75.3	toluene	8	16	0.13
1.59	6.3	BA	4.56	35.6	6.15	41.9	toluene	6	28	0.15
2.82	11.2	ST	6.63	63.6	9.45	74.8	none	—	39	0.29

(a) Monomer (2H5P) recovered unchanged (m.p. 124°C)

(b) 0.5% intolerance, 25°C.

TABLE 2

¹³C NMR Chemical Shift Data Spectra of 2(2-Hydroxy-5-Substituted Phenyl)2H-Benzotriazole

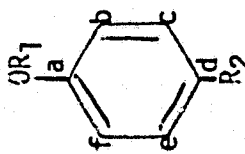
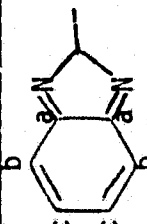
Group Assignment	Chemical Shift	2H5A			2A5A			2H5PR			2H5P		
		Int	CS	Int	Int	CS	Int	Int	CS	Int	Int	CS	
	a	47	153.64	22	146.27	25	148.37	31	149.06				
	b	60	122.07	60	125.67	53	118.78	70	118.64				
	c	107	128.12	56	129.39	48	126.92	75	127.39				
	d	31	129.77	35	144.82	100	127.69	124	127.49				
	e	44	119.15	123	127.50	97	117.68	61	117.91				
	f	9	124.74	19	132.87	9	124.69	14	124.69				
	a	25	142.76	31	135.51	23	142.81	25	142.62				
	b	113	117.67	125	118.26	45	117.29	125	117.51				
	c	60	130.32	70	125.32	19	141.44	24	133.24				
COCH ₃		50	26.33	60	26.43								
CO		26	195.54	25	195.37								
CH ₃ C=CH ₂								27	141.54				
CH ₃ C=CH ₂								58	21.77				
CH ₃ C=CH ₃								64	111.71				
O ⁰ CH ₃				25	168.53								
O ⁰ CH ₃				52	20.81								
CH ₃ -CH-CH ₃ OH						73	31.79						

TABLE 1 (continued)

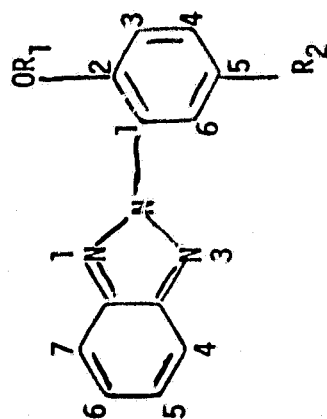
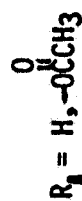
Compound	Benzotriazole Group		OH	CH ₃ -C=C-Ha				Hc-C=C-Ha			
	5,6H	4,7H		CH ₃	a	b		a	b	c	
2H5A	7.23-7.53(m)	7.7-8.0(m)	11.67(s)								
2A5A	7.2-7.5(m)	7.7-8.0(m)									
2H5PR	7.2-7.6(m)	7.75-8.06(m)	11.30(s)								
2H5P	7.2-7.6(m)	7.7-8.1(m)	11.33(s)	2.22(s)	5.11(t)	5.44(t)					
2A5E	7.36-7.68(m)	7.9-8.13(m)									
2H5V	7.20-7.6(m)	7.7-8.10(m)	11.40(s)					5.22(d)	5.72(d)	6.78(d)	

m - multiplet
s - singlet
d - doublet
t - triplet

TABLE 1

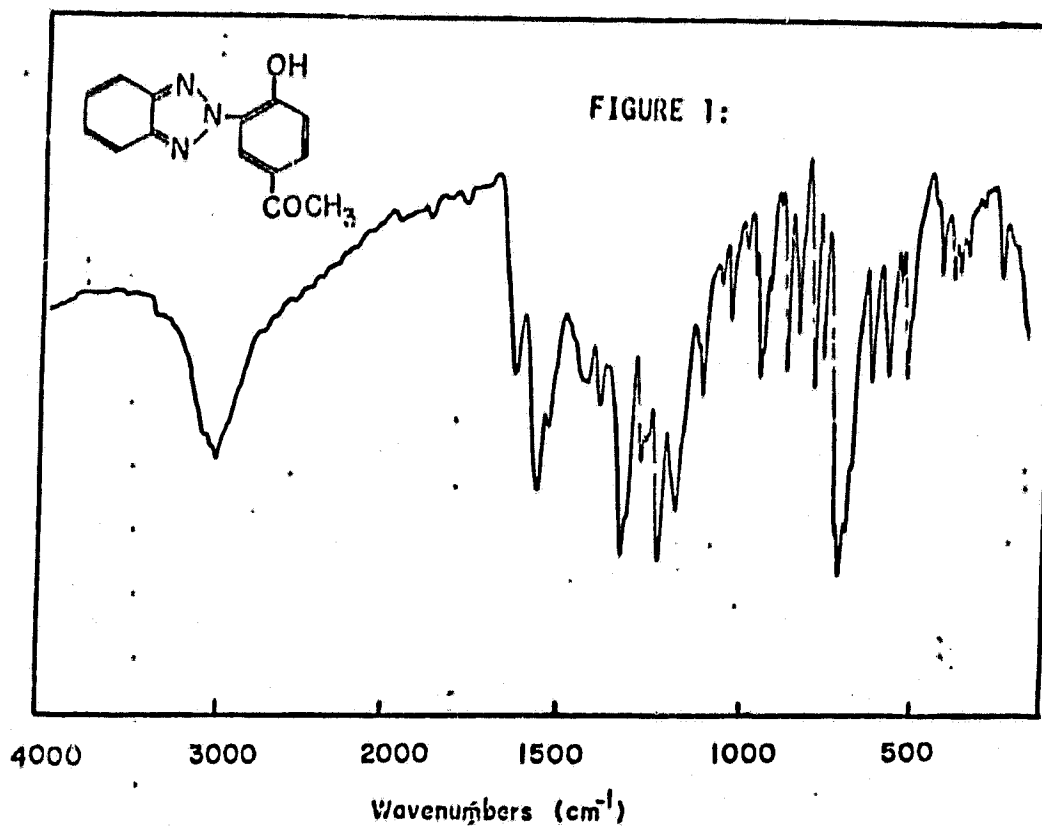
¹H NMR Chemical Shift Data of 2(2-Hydroxy-5-Substituted Phenyl)2H-Benzotriazole Derivatives

Compound	-COCH ₃	-OCOCH ₃	CH(CH ₃)OH	CHCH ₃ OH	CHCH ₃ OH	(CH ₃) ₂ COH	(CH ₃) ₂ COH	2-Hydroxyphenyl Group		
								3H	4H	6H
2H5A	2.60(s)							7.10(d)	7.41(d)	8.88(d)
2A5A	2.57(s)	2.25(s)						7.31(d)	7.41(d)	8.67(d)
2H5PR						1.63(s)	2.13(s)	7.10(d)	7.35(d)	8.58(d)
2H5P								7.14(d)	7.44(d)	8.45(d)
2A5E		2.32(s)	1.53(d)	5.05(q)	2.58(s)			7.29(d)	7.47(d)	8.23(d)
2H5V								7.13(d)	7.44(d)	8.41(d)

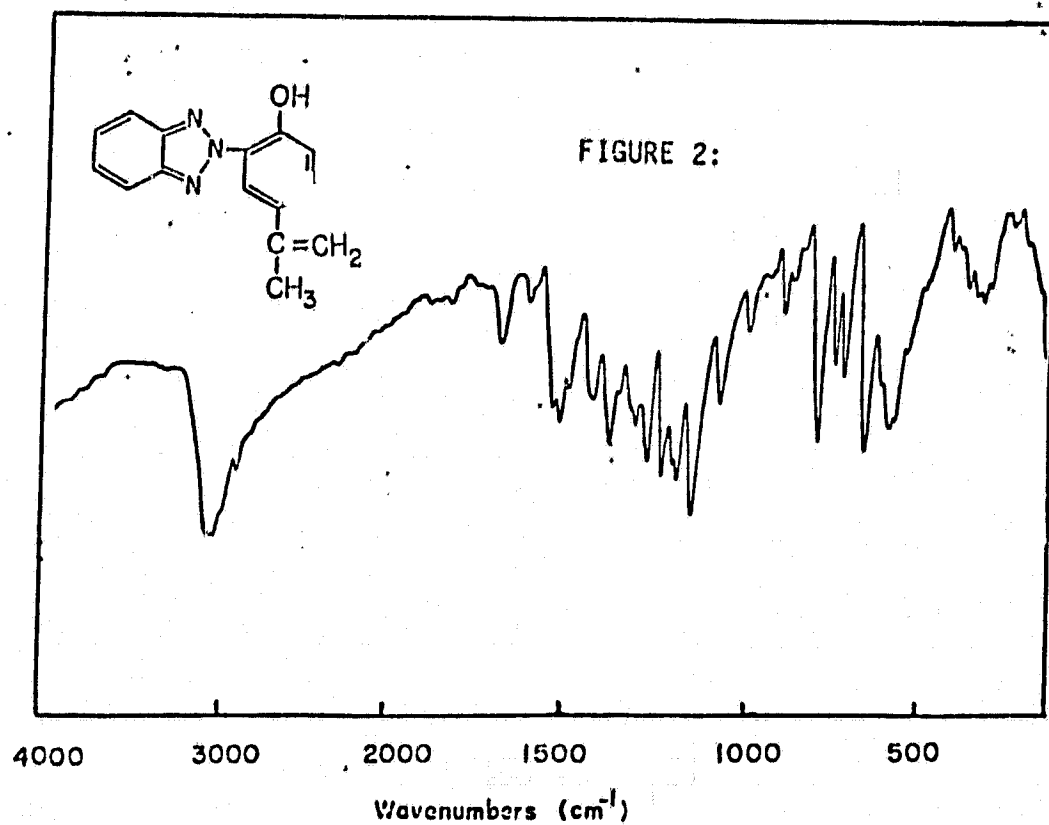


s - singlet
d - doublet

q - quartet

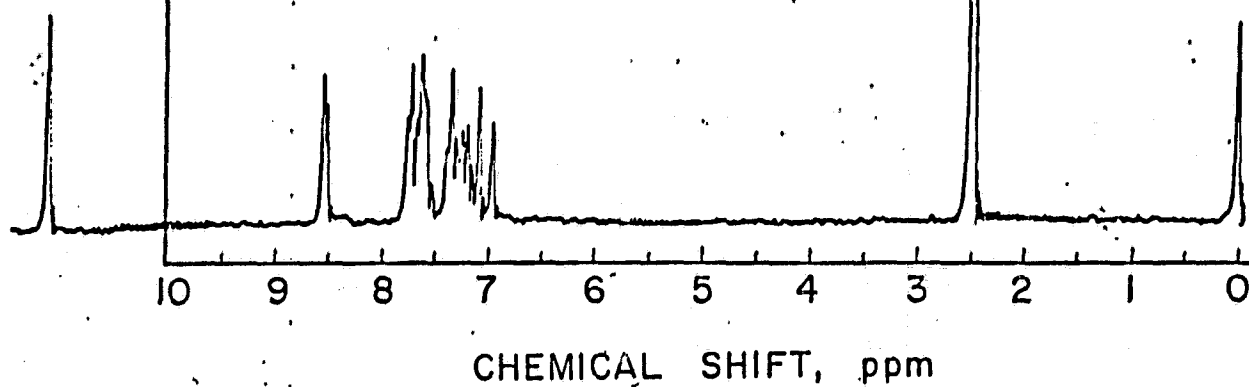
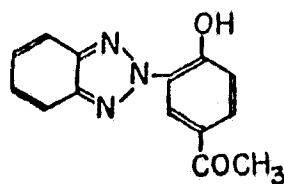


IR Spectrum of 2(2-Hydroxy-5-Acetylphenyl)2H-Benzotriazole (2H5A)



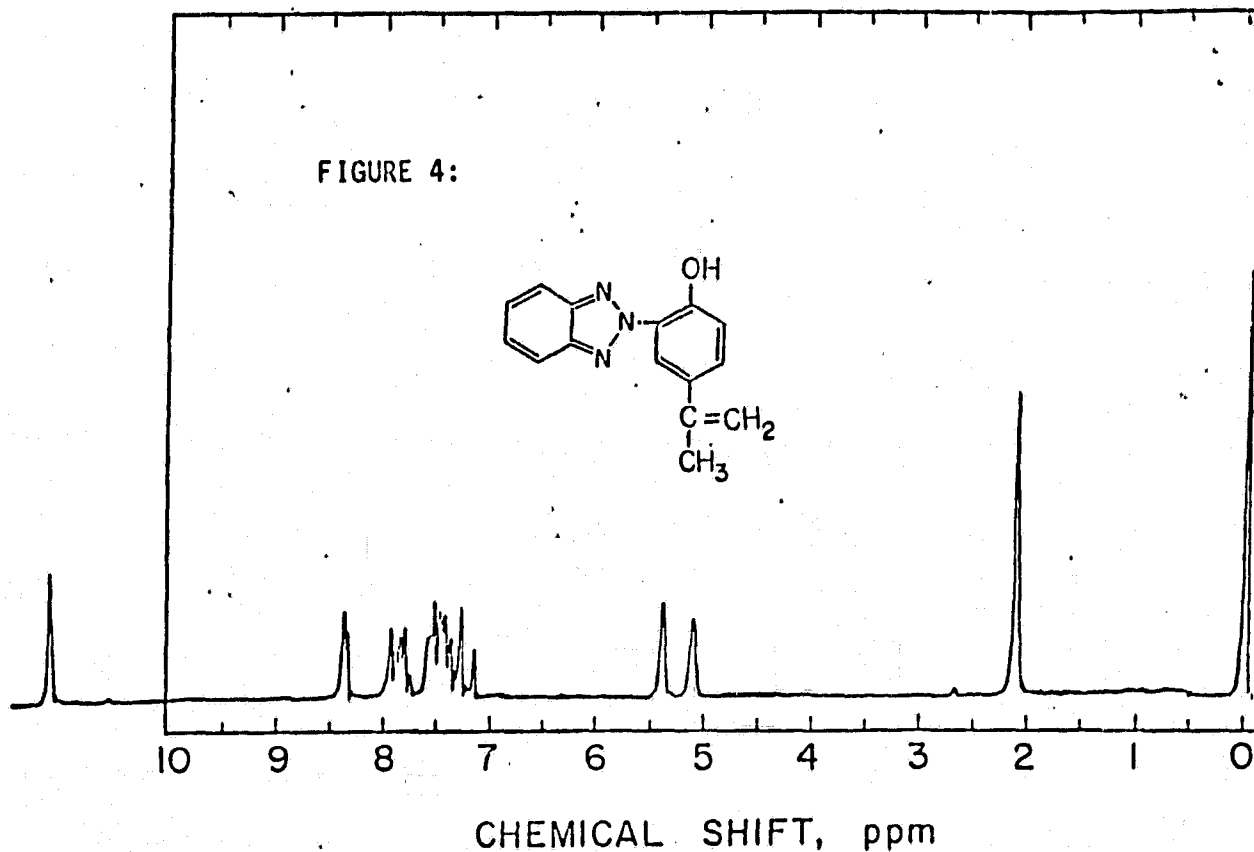
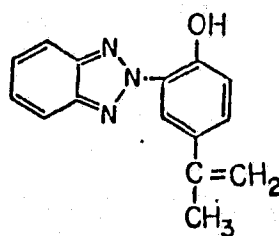
IR Spectrum of 2(2-Hydroxy-5-Isopropenylphenyl)2H-Benzotriazole (2H5P)

FIGURE 3:



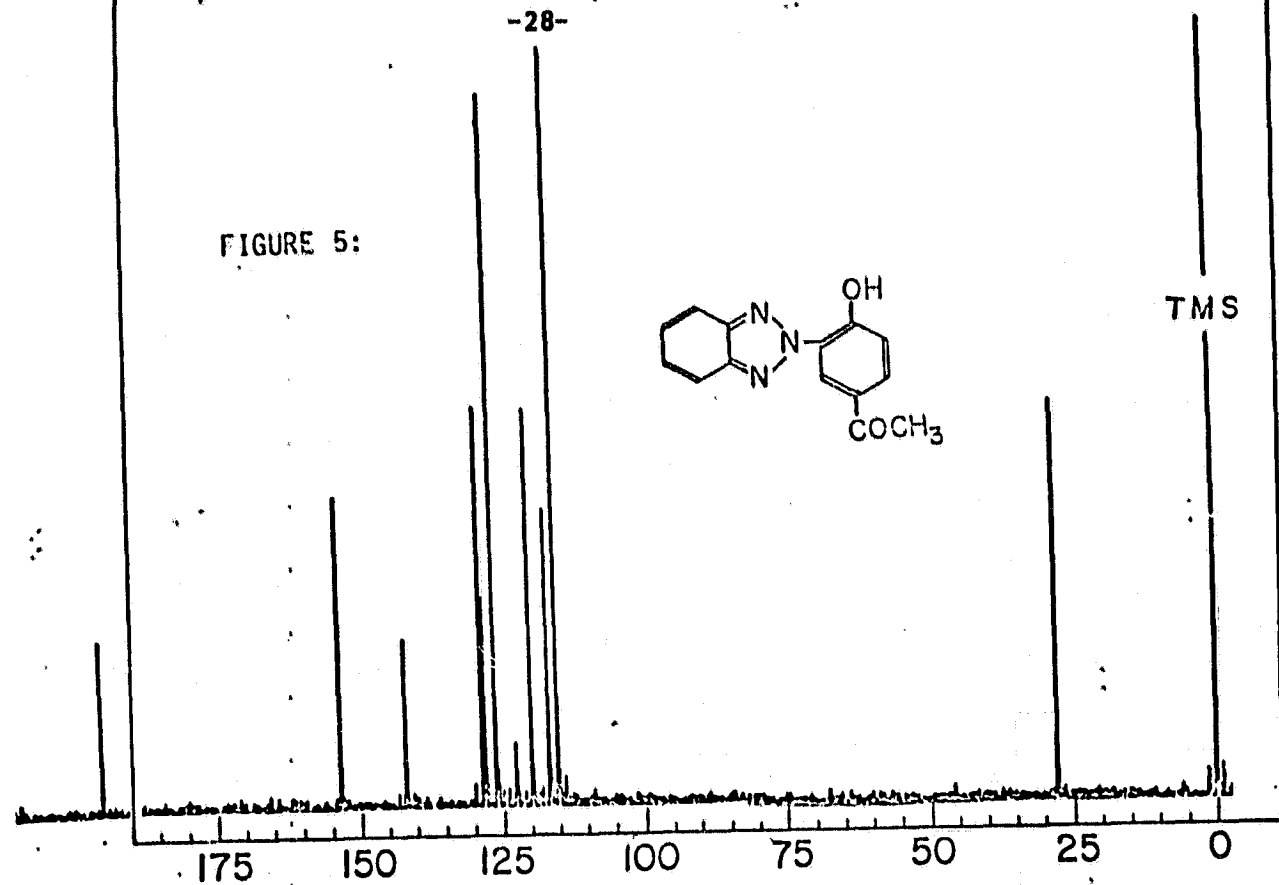
^1H NMR Spectrum of 2(2-Hydroxy-5-Acetylphenyl)2H-Benzotriazole (2H5A)

FIGURE 4:



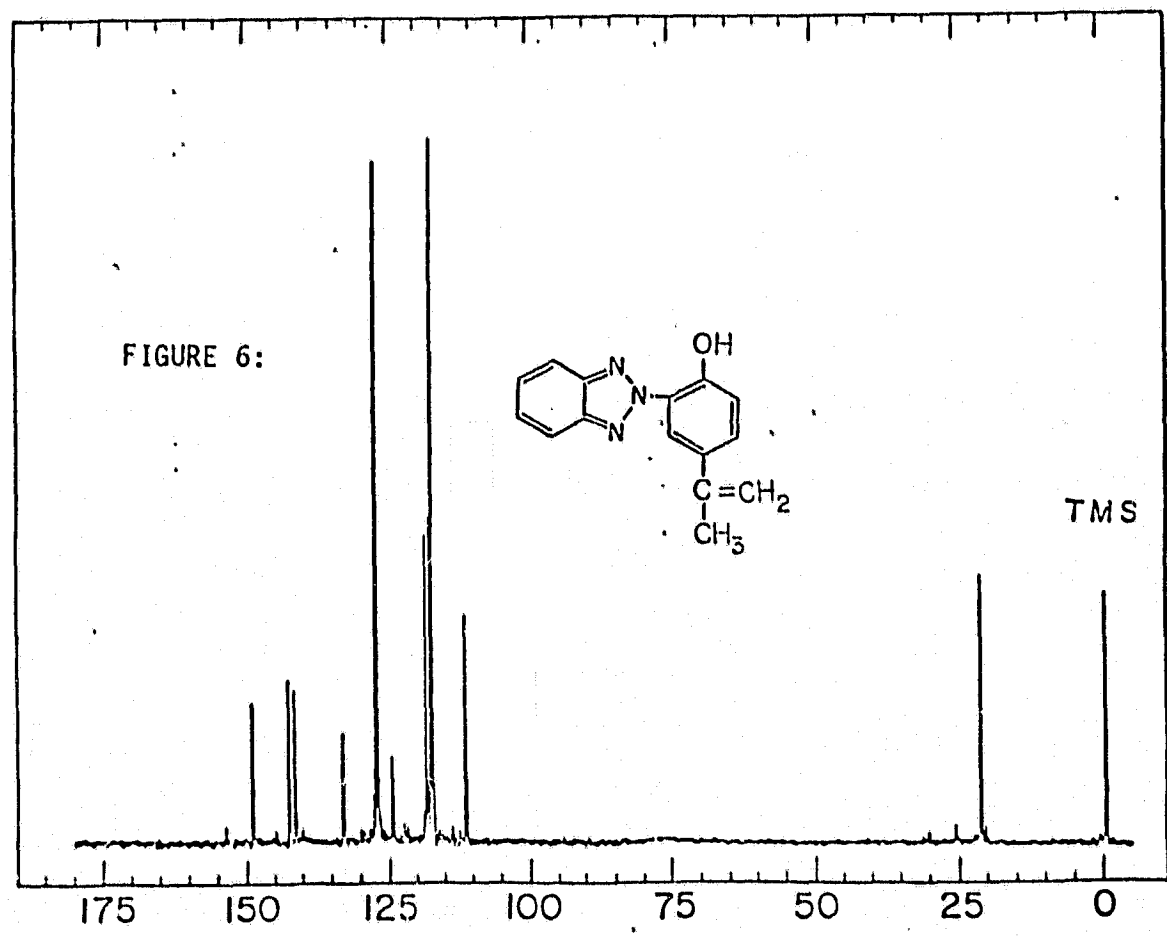
^1H NMR Spectrum of 2(2-Hydroxy-5-Isopropenylphenyl)2H-Benzotriazole (2H5P)

FIGURE 5:

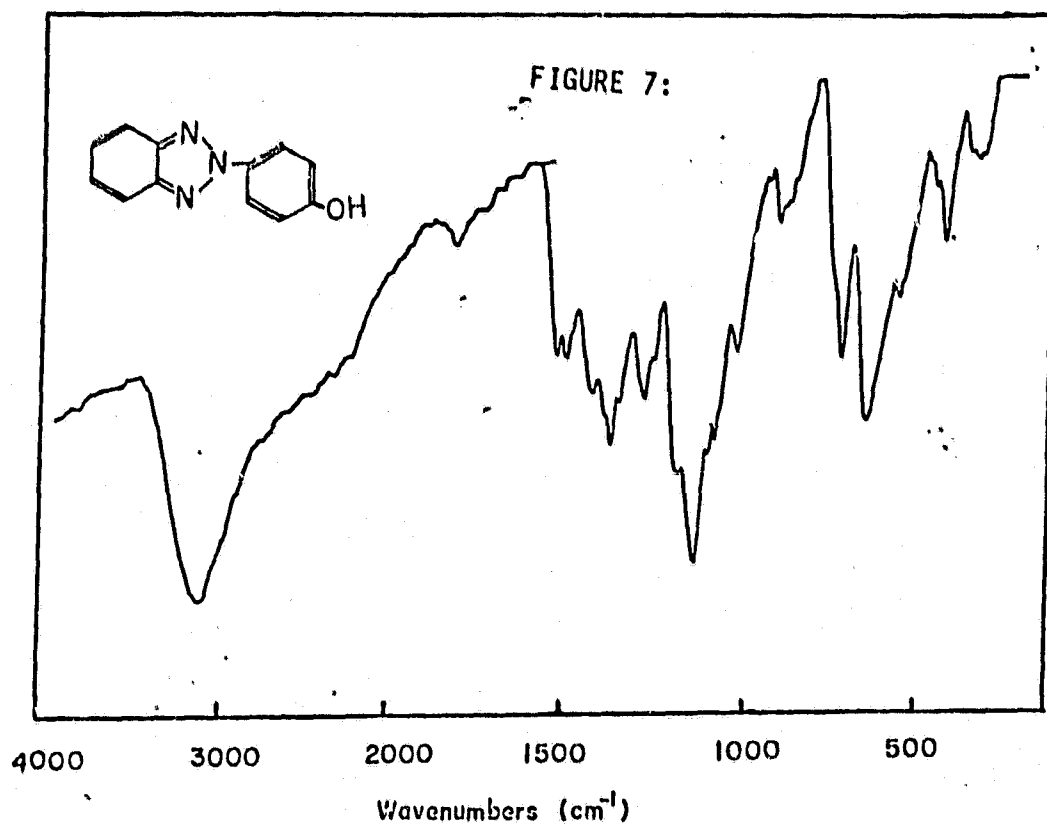


¹³C NMR Spectrum of 2(2-Hydroxy-5-Acetylphenyl)2H-Benzotriazole (2H5A)

FIGURE 6:



¹³C NMR Spectrum of 2(2-Hydroxy-5-Isonoprenylphenyl)2H-Benzotriazole (2H5P)



IR Spectrum of 2(4-Hydroxyphenyl)2H-Benzotriazole (4H)